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Arsenic contamination and accumulation in soil, groundwater and wild plant species from Qorveh County, Iran

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Abstract. The present study has been performed with the following objectives: (1) to determine the arsenic (As) concentrations in water, soil and leaves of plants growing in contaminated areas; (2) to evaluate the potential risk of arsenic in the Qorveh area and (3) to correlate the arsenic concentrations in water, soil and plants. To assess the potential of the native plant species for phytoremediation, plant, soil and water samples were collected from three contaminated villages of Qorveh County. The areas were the Babagorgor, Mehdikhan and Hajiabad (Qorveh county), and samples were taken from May to December 2012. Water samples were collected from 18 as contaminated shallow wells of Babagorgor, Mehdikhan and Hajiabad villages which were used for drinking and irrigation. The soil sampling period was from May to December 2012 (eight months) that were collected from three As-contaminated areas (20 samples per each area). Plants were sampled from As-contaminated areas in Qorveh county. The plant samples collected from the same location as the soil samples. Arsenic concentration in water samples ranged from 16.31 to 1233.01µg/L which correlated with alkalinity; total dissolved solid, total hardness chloride, electrical conductivity, calcium, sodium, sulphate and bicarbonate, (p≤0.001). Total arsenic in soils ranged from 172 to 1635 mg/kg. Collected plants had low arsenic concentrations, especially among the most common wild species. Among all plant samples, *Typha latifolia* was the most effective foliar accumulator of arsenic. This study revealed a correlation between arsenic levels in soils and the tested plants. Furthermore, the ability of plants to accumulate the arsenic, expressed by their biological accumulation coefficients and arsenic transfer factors, were found to be independent of the concentrations of arsenic.

Key words: arsenic contamination, Qorveh County, *Typha latifolia*, arsenic transfer factor.

Introduction

Phytoremediation is a new method that uses plants to assimilate or detoxify metals and organic chemicals. The mentioned term was first used in 1991 to explain the use of green plants to accumulate metals from groundwater and soil (Licht et al. 1995). In some studies, important role of phytoremediation were mentioned (Raskin et al. 1994). Even though, microorganisms have also been tested for remediation potential (Ahmann et al. 1997), plants have demonstrated the greater capacities to withstand and assimilate high concentrations of toxic metals and chemicals (Karimi et al. 2013). Plants that accumulate metals to high concentrations are referred as "hyperaccumulators". *Pteris vittata* (Chinese brake fern), the first reported arsenic (As) hyperaccumulating plant, can be potentially applied in the phytoremediation of As-contaminated sites (Ma et al. 2001, Fayiga et al. 2005). Phytoremediation has been considered for As contaminated areas; it can provide low cost, aesthetically pleasing options for cleaning up contaminated environment with As toxic metals (Karimi et al. 2010, Karimi et al. 2013).

For long, Kurdistan Province of Iran in some of its districts has been facing with the problem of As contamination. For instance, some villages which are located in northeast of Kurdistan, in Bijar and Qorveh Counties, the villages drinking and irrigation water has been contaminated with naturally occurring As. Since the groundwater is the main source of drinking and irrigation, contaminated water cause a serious treats to local people's health and harvested crops contamination with As. So, the contaminated irrigation water represents a major constraint in both Bijar and Qorveh counties, As contamination level of groundwater reaches up to to 400 µg/L (Zandsalimi et al. 2011). Therefore, the use of both surface and groundwater as source of water for domestic use in As contaminated areas, rises significant human health concern. For example, a survey that was conducted in 2010 on mentioned areas revealed that there were 180 cases of skin disorders related to As (Barati et al. 2012). In spite of several investigations on the occurrence of arsenic in drinking water in Qorveh county and the resulting poisoning of the mentioned habitants (Barati et al. 2012), there is no information about bioaccumulation ability of native endemic plant species of these contaminated areas. Therefore, the present study performed with the following objectives: (1) to determine the As concentrations in water, soil and leaves of endemic plants growing in highly As contaminated areas in order to determine the degrees of environmental contamination level; (2) to find bioremediation ability of native endemic plant species growing in As contaminated areas.

Material and methods

Study Area

Kurdistan Province is located at West of Iran, bordering Iraq from 34° 442ʹ to 36° 302ʹ North, and, 45° 312ʹ to 48° 162ʹ East. This state is one of the most mountainous provinces of Iran and has a generally cold climate. Kurdistan Province represents about 1.7 % of the area of the entire country and has more than, 450,000 inhabitants. At the east of state, there are some villages in Qorveh County (a 2430 km^2 area with an average altitude of about 1790 m above sea level) where drinking water has been contaminated with naturally-occurring As (Mosaferi et al. 2005).

Soil Sampling and Analysis

Soil was collected from May to December 2012 from three As-contaminated areas (20 samples per area). Three separate ways were used for soil sampling. First, surface soil samples were taken at different distance (0, 400 and 800m) from the contaminated shallow well of each village to determine the extent of As contamination. Second, samples were collected from different depth (surface and subsurface). Third, soil attached to plant roots (rhizosphere soil) was sampled to determine the bioaccumulation factor of each plant species which were collected from the study area.

The soil samples (500 g) were dried at 60 ºC for 12 h, mixed, homogenized and sieved through a 2mm grid. Soil properties were determined as follows: pH was determined potentiometrically in a soil paste saturated with water; organic matter was determined by dichromate oxidation using the Tiurin method (Soon & Abboud 1991); also, cation exchange capacity (CEC) according to the ammonium acetate method by extracting with a 1.0 mol of NH_4OAc solution (pH 7.0) was determined; and particle size distribution (sand, silt, and clay) analyzed by the pipette method (Ashworth et al. 2001).

Analysis of As in Soil Samples

The finely powdered and homogenized soil samples (0.5 g) were digested with 10 ml of a 3:1 HCl: HNO3 mixture in a Kjeldahl digestion tube. Tubes were left overnight at room temperature and then placed in a heating block. Each was covered with an air condenser and refluxed gently at 80 ºC for 2 h. After cooling, the digests were filtered through a moistened Whatman No. 40 filter paper into a 50 ml volumetric flask and 10 ml of a solution containing 10 % HCl, 5 % ascorbic acid and 10 % KI was added. Then, distilled water was added up to flask volumetric line. The concentrations of As was determined using the atomic absorption spectrophotometry (Shimadzu AA-680). Reference standard for calibration of the AAS was made using 1000 mg l^{-1} (Beach leaves material FD8, Commission of the European Communities, Joint Research Centre ISPRA).

Plant Sampling and Analysis

Plants (at the flowering stage, where possible) were sampled from As-contaminated areas in Qorveh county. For small plants the whole plants were taken, but only plant species which were found frequently in the study areas and/or had a high shoot biomass collected. A total of 61 plant samples belonging to 13 different species were collected. Only the aerial parts of the plants (stems, branches and leaves) were collected; the roots were not sampled. Plant samples were washed with tap water, rinsed with deionized water and oven-dried at 55ºC for 72h. They were digested as described by Meharg & Jardin (2003). Analysis of As was performed by atomic absorption spectrophotometry, as described above.

Results

Arsenic in Groundwater

The Physicochemical properties of contaminated water of shallow wells in three villages of Qorveh County were measured (Table 1). Consequently, as data shows, the hardness and the As contamination values were high. So, the water sources were classified into hard and very hard water (total hardness: $CaCo_3$ >170 mg/L in water samples). As Table 1 show, Hajiabad water samples had the lowest levels of hardness and TDS, while Babagorgor water samples had the highest levels of hardness and TDS. Conspicuously, all the shallow wells sampled in this study, had As concentrations higher than the WHO drinking water standard of 10 µg/L (WHO 1993). Also, the pH of groundwater samples ranged from 6.89 to 8.24 and the EC ranged from 589 to 792 ds/m. Also, Table 1 illustrates major relationship between As levels and sodium, calcium, bicarbonate, chloride, TDS, EC, and pH in water samples ($p \leq 0.001$). Whereas, the highest affiliation were between As and TDS (R=0.81). Furthermore, As concentration of Babagorgor shallow wells was very high (1233.01 µg/L), almost 120 time greater than the WHO standard of drinking water (10 µg/L) (WHO, 1996).

Soil Characteristics

Soil texture, organic matter, pH and Block-Distance away from source; Depth profiles-Total As in soil samples (mg/kg) and some other edaphic parameters of the contaminated soils of three villages in Qorveh County were measured (Table 2). The pH was alkaline in area C, while it was neutral in area A and B. Also, low levels of phosphate in the soil sampling sites were considerable. Subsequently, analysis of soil texture showed significant differences between sampling sites, particularly in regard to the clay and silt fractions ($p<0.05$). The silt content in B area was much higher than of clay, while the opposite pattern was found in area A (Table 2). Also, there wasn't any significant differences between silts and total P in all three sampling sites ($p<0.05$).

Arsenic in Soil

The area around the shallow well in Babagorgor (area A; Table 2) had the highest concentrations of As. The level of As concentrations in soil of area A and B were much higher than the average toxicity threshold of 40 mg/kg established for crops plants as reported by Sheppard (1992). Area C (Hajiabad) had much lower level of As concentrations than Babagorgor and Mehdichan. In spite of sampling up to a considerable distance from the wells, there wasn't any decline in As concentration in depth profiles soil samples (Samples are taken from 0 to 20 cm and 20 to 40 cm in depths) (Table 2).

Arsenic in plants

A total of 13 plant species belonging to 9 families were sampled (Table 3). Plants in area C demonstrated very low As concentrations, occasionally below the limit of instrumental detection (Table 3). In area B, plant species had higher As concentration, usually above 4 mg/kg (11 out of 13), but only *Typha latifolia* showed significant accumulation, with 92.23 mg/kg of As in its leaves (Table 2). Of the 13 plant species sampled in area A, 7 species had more than 10 mg/kg of As in their leaves, with *Typha latifolia* as the best As accumulator (76.70 mg/kg).

Relationship between the As concentrations in ground-

Table 1. Physicochemical properties of shallow wells from three contaminated areas in Qorveh County (* = Mean).

Location	As (µg/L)	K (meq/L)	Na (meq/L)	Ca (meq/L)	Mg (meq/L)	HCO_3 (meq/L)	Cl (meq/L)	NO_3 (meq/L)	EC (ds/m)	pH	TDS (mg/L)	SAR	Hardness (mg/L $CaCO_3$)
Babagorgor (Area A)	1233.01*	0.17	0.614	1.812	7.922	7.449	0.51	0.15	792.22	6.89	538.28	0.14	260.11
Mehdichan (Area B)	573.4	0.077	0.052	1.720	6.931	6.730	1.33	0.2	981.95	7.43	437.01	0.07	181.74
Hajiabad (Area C)	16.31	0.032	0.044	4.120	3.528	3.527	1.5	0.38	589.87	8.24	299.84	0.29	136.92

Table 2. Arsenic concentration and some edaphic parameters in the three contaminated areas in Qorveh County. Block-Distance away from source; Depth profiles-Total As in soil samples (mg/kg) (*= Mean±SE).

Location	Block	Total As in soil samples (mg/kg)		Soil texture (%)			pH	EC (ds/m)	OM (mg/kg)	Total P (mg/kg)
		0-20	20-40	Sand	Silt	Clay				
Babagorgor	0	1328.43*±185.97	1635.41*±193.93	49.61	16.18	27.98	7.08	2.45	1.07	24.91
	400m	1130.91±177.62	1378.87±179.41	55.11	19.01	25.03	7.81	0.91	1.75	27.30
	800m	812.77±136.93	994.65±126.73	48.55	25.25	23.51	7.86	1.01	1.61	15.05
Mehdichan	0	1207.12±114.83	1417.51±131.62	47.93	23.85	14.01	7.83	0.84	2.09	14.87
	400	1125.10±168.99	1494.57±144.75	39.81	27.06	21.46	7.92	2.19	2.86	25.81
	800m	1100.52±114.53	1318.29±139.46	54.01	16.95	18.23	7.94	0.91	2.38	13.75
Hajiabad	0	414.03±44.83	408.19±52.48	61.34	19.22	20.51	8.01	1.66	1.70	9.13
	400m	168.98±36.35	175.92±48.42	59.69	26.48	20.82	8.47	1.43	1.88	8.99
	800m	164.02±15.06	172.61±21.77	55.87	19.98	21.14	8.72	1.92	1.51	4.93

Table 3. Arsenic concentration in leaves of plant samples collected from three contaminated areas in Qorveh County (*All data are presented in mean±SE; ND = Not Detectable; (A=Babagorgor, B=Mehdichan, C=Hajiabad))

Family	Scientific Name	No.sample	Total As (mg/kg)		
			A	B	C
Asteraceae	*Lactus serriola*	4	7.91±0.7	4.94±0.8	2.01±0.6
Asteraceae	*Chondrilla juncaceae*	5	19.01±5.1	16.14±1.5	14.32±0.5
Asparagaceas	*Asparagus Spp.*	11	5.19±0.8	7.42±0.8	0.11±0.07
Brassicaceae	*Raphanus Spp.*	12	23.91±0.6	11.44±0.2	9.40±0.09
Brassicaceae	*Descurainia Sophia*	6	27.79±2.1	14.94±0.6	9.16±0.5
Compositae	*Acroptilon repens*	10	16.31±3.8	10.16±1.9	10.01±0.03
Fabaceae	*Melilotus officinalis*	2	9.94±0.8	ND	6.15±0.06
Fabaceae	*Alhagi persarum*	3	ND	19.43±1.9	8.42±0.32
Fabaceae	*Medicago sativa*	10	ND	6.71±0.5	5.04±0.05
Laminaceae	*Mentha longifolia*	4	17.35±0.5	ND	0.7±0.04
Poaceae	*Elymus Spp.*	7	9.15±0.6	6.19±0.6	4.91±0.08
Solanaceae	*Lycopersium esculentum*	8	25.21±2.5	18.92±1.4	6.51±0.06
Typhacea	*Typha latifolia*	15	76.69±0.8	92.23±7.4	10.89±0.7

water and surface soils: The As concentration of surface soil and groundwater were from 172 to 1635 mg/kg and 16.31 to 1233.01 µg/L respectively. Also, the As concentration of surface soil tended to increase with increasing As concentration of groundwater with linear regression coefficients of 0.051 ($p \leq 0.05$), 0.0121 ($p \leq 0.01$) and 0.14 ($p \leq 0.01$), for Babagorgor, Mehdichan and Hajiabad.

Relationship between the As concentrations in plant species and surface soils.

Figure 1 shows the relationship between As concentrations of plant leaves and surface soils at three studied sites in Qorveh county. In general, data indicate that there is no meaningful predicative capability between soil concentrations and plant concentrations of As in plant species of Babagorgor, Mehdichan, Hajiabad (Fig. 1), with linear regression coefficients of 0.06 ($p \leq 0.05$), 0.019 ($p \leq 0.01$) and 0.103 ($p \leq 0.01$), respectively. The shoot As (mg/kg dry wt) to total soil As (mg/kg dry wt) was used as an indication of As transfer coefficient (AsTC). In this investigation, AsTC were in the ranges 0f 0.002-0.053 (Fig. 2).

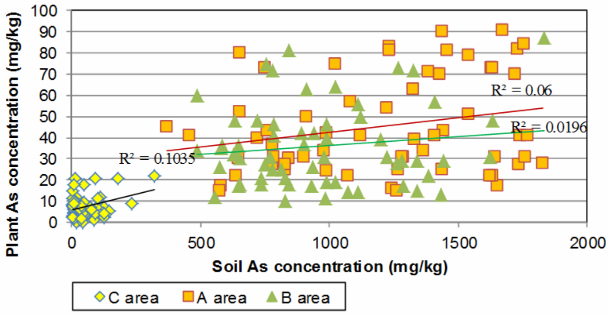

Figure 1. Relationship between Arsenic concentrations in plant leaves and surface soils from three contaminated areas in Qorveh County.

Discussion

In some villages in Bijar and Qorveh districts, natural contamination of groundwaters with As, has been recognized.

Excessive concentrations of As in drinking water and their uptake by plants and subsequent introduction into the food chain is a potential risk to human health (Barati et al., 2012). This investigation illustrated that people in the Kurdistan Province may be overexposed not only to As, but also to NO_3^- from groundwater (Table 1). Harmful effects on the health may be prominent in the coming years for the local population. The comparing As concentration in the main plant groups that have naturally grown on As-contaminated areas is useful in this study. This data are may be regarding measurement of the risk that natural processes may pose to

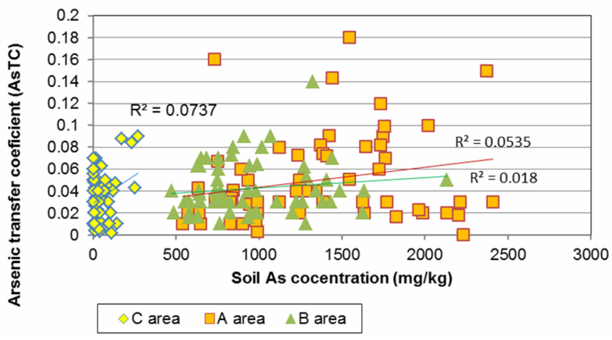

Figure 2. Soil-shoot transfer coefficient (AsTC) plotted against total soil As concentration (0-10cm) for samples from 3 contaminated areas in Qorveh County.

the environment in contaminated area.

Mean total As concentration in the soil in area B and C ranged from 1318.29 to 1494.57 and 172.61 to 408.19 mg/kg respectively. Also, mean As concentrations of all sampled sites were higher than the average toxicity threshold of 40 mg/kg established for agricultural soil (Sheppard 1992). The bioavailability and toxicity of As and other metals in soil are related to various soil parameters. Effects of soil factor in As accumulation by plants is important, but these effects depends on species type (Davis et al. 2001). This investigation demonstrates that the regular use of As contaminated groundwater for irrigation of agriculture land can potentially lead to human intake of As.

Since As concentration in the soil samples for the study area were lower, this will be consistent with the idea that the soil to shoot As transfer coefficient is appear independent of the soil As concentrations. The effects of the soil source, pedological factors (pH, EC, organic matter and colloid contents, soil texture, minerals and drainage conditions), chemical speciation, plant species, age and part of plants on the As uptake by plants are well known (Meharg & Macnair 1990, Casado et al. 2007, Singh 2007).

The soil to shoot As transfer coefficients was in the range of 0.010 to 0.053. Arsenic transfer coefficient (AsTC) ratio can be used to evaluate the As bioaccumulation (BA) capacity of plants. This ratio in Figure 2 ranged from 0.002 to 0.18 with a mean value of 0.049 in area A and mean values of 0.042 and 0.034 in areas B and C respectively. In spite of the presence of elevated soil As, these values were within the typical range for non-polluted soils (Sheppard, 1992). These data illustrate not meaningful soil plant transfer of As that is not effected by soil As concentration and soil As source. Although among plant species studies, there are variations in their AsTC values particularly for *Typha latifolia*. This suggests to the authors that it can be used as a possible phytoremediator.

Samples generally exhibited As contents that were weakly correlated to that of the soil As samples. Amount of pH, P, organic matter and soil texture, had no effect on soil As concentration and its bioavailability to plants. Even though the concentrations of As in the plants were low, in the most contaminated conditions, however *Typha latifolia* was significantly higher. In spite of the long history of this contaminated area, there is a prominent scarcity of effective pressure tended As tolerance by the plant species through the As accumulation. Therefore, it is maybe that plants play a minor role in superficial geochemical cycling of arsenic. Finally, this study illustrates the necessary of a more investigation of As contents in crops, fodders and vegetables.

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